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Title: PROCESS FOR THE SELECTIVE DESULFURIZATION OF OLEFINIC CUTS ;

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ABSTRACT:

Hydrocarbon cuts of high olefin content are desulfurized, without substantial loss in octane number, by reaction with hydrogen in the presence of a catalyst comprising (a) a specified non-acidic carrier and (b) cobalt and at least one of tungsten and molybdenum, the atomic ratio being higher than 0.55.

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(54) Catalyst for the selective
desulfurization of olefinic cuts

(57) Hydrocarbon cuts of high olefin
content are desulfurized, without
substantial loss in octane number, by
reaction with hydrogen in the
presence of a catalyst comprising (a) a
specified non-acidic carrier and (b)

cobalt and at least one of tungsten
and molybdenum, the atomic ratio

$$R = \frac{\text{cobalt}}{\text{cobalt} + (\text{molybdenum and/or tungsten})}$$

being higher than 0.55.

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SPECIFICATION

Process and catalyst for the selective desulfurization of olefinic cuts

The present invention is concerned with a process and a group of catalysts for hydrodesulfurizing hydrocarbon cuts of high olefin content (15 to 45% of olefins by weight), this hydrodesulfurization taking place with minimum hydrogenation of the olefins, so as to avoid as far as possible a substantial loss in octane number when the hydrocarbon cut is to be used as a gasoline.

Certain gasolines obtained by catalytic cracking may have, even after extraction or chemical removal of the thiols, a too high content of non-acidic sulfur compound to satisfy market requirements. This is the case with the catalytic cracking gasolines obtained from vacuum distillates or deasphalted residues of high sulfur content. In that case, the resultant gasolines have a high content, not only of thiols but also of non-acidic sulfur compounds of the sulfide, di-sulfide, thiophene and alkyl-thiophene type, which must be at least partly removed without concomitantly decreasing the desired octane rating for the resultant fuel.

Conventional hydrodesulfurization catalysts that comprise metals and/or sulfides of metals from groups VIII and VI A of the Mendeleeff periodical classification in which the atomic ratio R, which is defined by the equation $R = \text{VIII}/(\text{VIA} + \text{VIII})$, is lower than 0.5, preferably about 0.25, are known as very active for hydrogenating olefins. It has however been surprisingly found that catalysts of the above groups comprising cobalt, together with molybdenum and/or tungsten, can desulfurize efficiently a catalytic cracking effluent, without substantially hydrogenating the olefins present in this effluent, provided that

$$R = \frac{\text{Cobalt}}{\text{cobalt} + (\text{molybdenum and/or tungsten})}$$

calculated in atoms of the three metals, is higher than 0.55, preferably in the range from 0.6 to 0.9 and more particularly in the range from 0.7 to 0.8. On the other hand, in order to avoid parasitic polymerization of the olefins through a mechanism of the carbonium ion type (which polymerization would be detrimental to the stability of the catalyst), it is necessary, when manufacturing the catalyst, to deposit the cobalt and molybdenum compounds or the cobalt and tungsten compounds onto a non-acidic carrier; the carrier will then be (a) silica; (b) an alumina of specific surface lower than 70 m²/g and of the α -alumina or tetragonal γ -alumina type (obtained for example, by heating cubic γ -alumina in an autoclave); (c) a carrier of the cobalt, nickel, barium, magnesium or calcium aluminate type having a specific surface lower than 130 m²/g, preferably calcium aluminate, (d) an alumina previously heated in an autoclave and whose specific surface is lower than 135 m²/g. The catalysts resulting from use of a carrier from group (b) or (c) will themselves have specific surfaces lower than 70 and 130 m²/g respectively.

The total content, expressed by weight, of the oxides of cobalt, molybdenum and tungsten (i.e. the metals deposited on the carrier, and sometimes also present within the carrier, when using, for example, cobalt aluminate) is between 2 and 30% and preferably between 8 and 25%, these amounts of cobalt, molybdenum and/or tungsten being the amounts of the metals deposited on the carrier and, if any, present in the carrier. The process thus avoids substantially decreasing the octane number of the catalytic cracking effluent and decreasing the initial bromine number of this effluent by more than 10%: the decrease may be as low as 8%.

The feedstocks used in the process of the invention boil at least in major part in the gasoline range, for example below 210°C, especially below 200°C, and in some cases below 170°C, depending on the expected use for these cuts.

The catalysts may be prepared by the various methods disclosed in the prior art, for example, either by impregnating the carrier with a volume of a solution of salts of the selected metals (molybdenum, cobalt, tungsten) equal to the pore volume, or by mixing the selected carrier precursor, alumina powder or silica salt or aluminate (for example, calcium aluminate), with selected salts of the active agents and extruding the resultant paste. Among the cobalt, molybdenum and tungsten salts, soluble salts of these metals may be mentioned: the nitrate, sulfate or acetate of cobalt, ammonium hepta-molybdate or ammonium paratungstate of molybdenum and tungsten respectively. The impregnation may be effected in one or two steps; in the case of two impregnations, the latter are separated with drying and calcining; if the catalyst is prepared by mixing, and then extruding, the precursors of the active agents may be the above salts, or the oxides in the case of molybdenum and tungsten. After the impregnation or extrusion step, the catalysts are dried at a temperature of, for example, 100 to 150°C, and then calcined at, for example, 500°C in an air stream.

Before use, the catalyst is preferably subjected to sulfurization at a temperature 20 to 60 Centigrade degrees higher than the selected reaction temperature (preferably about 30 to 50 degrees higher) for a few hours by means of a mixture of hydrogen sulfide diluted in hydrogen (amount of hydrogen sulfide in hydrogen: 0.5 to 5% in volume) at an adequate space velocity of, for example, about 1000 to 3000 liters of gas at standard temperature and pressure per liter of catalyst per hour. The

resultant catalyst comprises between 0.5 and 25% of cobalt sulfide (usually in the form of Co_9S_8) and 0.5 to 25% of molybdenum or tungsten sulfide (usually as MoS_2 or WS_2).

- For treating olefinic gasolines containing sulfur and obtained from a catalytic cracking operation, the catalyst (which appears, for example, as extrudates or balls of an average equivalent diameter between 1.5 and 6 mm) is preferably used as a fixed bed in a reactor providing a concentration gradient. The hydrotreatment is performed at a temperature in the range 260 to 310°C; the pressure to be applied is usually between 10 and 60 bars and preferably between 20 and 40 bars; the space velocity, expressed as m^3 of injected charge per m^3 of catalyst per hour is usually between 2 and 15 and preferably between 4 and 8; the hydrogen partial pressure is usually between 5 and 50 bars and preferably between 10 and 40 bars. At the reactor outlet, the reaction mixture is cooled and the hydrocarbon fraction distilling in the gasoline range is condensed and then separated from a gas fraction of high hydrogen content which is, at least partly, recycled to the reactor (recycle gas). Irrespective of the nature of the charge, which is a catalytic cracking effluent, and which may have various sulfur contents, it is preferred that the hydrogen sulfide content of the recycle gas be not higher than 5000 parts per million by volume (5000 vpm) preferably not higher than 400 vpm; at higher values, it is necessary to increase the rate of purge or to remove by washing a portion of the hydrogen sulfide, so as to maintain the H_2S content of the recycle gas below 5000 or preferably 4000 vpm. In the possible case where the charge subjected to hydrodesulfurization has a very low sulfur content ($\text{S} < 50$ ppm), it is conversely necessary to reduce the purge rate, so as to maintain a hydrogen sulfide content of the recycle gas higher than 150 vpm, preferably higher than 200 vpm, so as to increase the selectivity of the catalyst system.

EXAMPLE 1

- A catalyst is manufactured by impregnating alumina balls having a 0.5% b.w. content of Na_2O , a specific surface of $87 \text{ m}^2/\text{g}$ and a total pore volume of $0.57 \text{ cm}^3/\text{g}$, according to the following procedure: 57 cm^3 of a solution of cobalt nitrate and ammonium paratungstate are added to 100 g of alumina balls having a diameter between 3 and 4 mm, at such concentrations that the resultant catalyst contains 6.3% of WO_3 and 6.0% of CoO (by weight) after drying and calcining for 3 hours at 500°C in an air stream of 25 l/hour. This catalyst is referred to as catalyst A. In this catalyst, $R = 0.75$.

- A second catalyst B is prepared from the same alumina as used in the above case; however two successive impregnations, separated by air-drying at 150°C and air-calcining (25 l/h) at 350°C, are effected. The first impregnation concerns tungsten, the second one cobalt; in the two operations, the impregnations are performed without excess of solution, i.e. by using 57 cm^3 of solution of the precursor salt for 100 g of alumina balls. After drying and a final calcination in the same conditions as with the catalyst A, there is obtained a catalyst containing 6.3% of tungsten oxide WO_3 and 6.0% of cobalt oxide CoO (by weight). In this catalyst, $R = 0.75$.

- A third catalyst C is prepared from the same alumina as used for preparing catalyst A and according to the same operating technique; however, the impregnation solution now contains ammonium heptamolybdate and cobalt nitrate in such proportions that, after drying and calcining, the catalyst contains 4.4% of molybdenum oxide MoO_3 and 7% of cobalt oxide CoO . In the catalyst C, $R = 0.75$.

- Three other catalysts D, E, F are prepared by the method used for the catalysts A and C; but with a different carrier consisting of silica having a specific surface of $150 \text{ m}^2/\text{g}$, for catalysts D and E, and a calcium aluminate of the SECAR cement type having a specific surface of $45 \text{ m}^2/\text{g}$, for the catalyst F. The specifications of the resultant catalysts are given in the Table I. $R = 0.75$ for the catalysts D, E and F.

- Two catalysts G and H are also prepared with the same alumina carrier as used when preparing the catalyst A and according to the same procedure; however the concentrations of the precursor salts are so adjusted that the atomic ratio R is now 0.325.

- Two catalysts I and I' are finally prepared from γ cubic alumina having a surface of $205 \text{ m}^2/\text{g}$ (boehmite), by a method comprising only one impregnation and by adjusting the precursor salts of cobalt and molybdenum so as to obtain a ratio R of 0.75 for the final catalyst I' and 0.325 for the final catalyst I.

TABLE I
Specifications of the catalysts employed

Nature of the Carrier / Specifications of the Resultant Catalysts	A	B	C	D	E	F	G	H	I	I'
	Tetragonal γ -Alumina with 0.5% b.w. Na_2O			Silica		**	Tetragonal γ -Alumina of Low Surface (0.5% Na_2O)		Pure Alumina of High Surface Ex. Boehmite	
Total pore volume (cm^3/g)	0.53	0.53	0.53	0.81	0.8	0.41	0.53	0.53	0.57	0.57
Specific surface (m^2/g)	62	62	62	143	137	43	62	62	183	183
Cobalt (% oxide b.w.)	6.0	6.0	7	7.0	6.0	7.0	3	2.5	3	7.0
Molybdenum (% oxide b.w.)	0	0	4.4	4.4	0	4.4	12	0	12	4.0
Tungsten (% oxide b.w.)	6.3	6.3	0	0	6.3	0	0	17.6	0	0

** Calcium aluminate (SECAR cement).

EXAMPLE 2

Catalytic cracking gasoline whose specifications are given below is treated with hydrogen:

	Distillation ASTM	
	Initial point (°C)	40
5	50% point (°C)	92
	Final point (°C)	190
	Volumic mass (g/ml)	0.734
	Bromine number	39
	Olefins % b.w.	19.4
10	Sulfur % b.w.	0.08
	Research octane number	92

Before starting the treatment, the catalysts are pre-sulfided at 320°C under a pressure of 4 bars for 4 hours with a gas mixture of hydrogen sulfide (2% by volume) diluted in hydrogen. The space velocity in the pre-sulfiding step is 2000 (in liters of gas at normal temperature and pressure per liter of catalyst per hour). After the pre-sulfiding step, the temperature is decreased to the value selected for the hydrodesulfurization operation, and the charge is supplied to the reaction zone. After pre-sulfiding, the sulfur content of the catalysts is 4.5% by weight.

The operating conditions, as defined in Table II are the same for all the catalysts. The results obtained after 120 hours of test are also reported in Table II. It is observed that the catalysts A, B, C, D, E and F, although exhibiting different levels of activity with respect to the hydrodesulfurization and the hydrogenation of the olefins, are however much more selective than the catalysts G, H and I (wherein the contents of metals from the groups VIII and VI A are in the atomic ratio of $R = 0.325$) or than the catalyst I' which has a satisfactory R ratio but whose carrier has a too high specific surface. The too high hydrogenation activity of the catalysts G, H and I must also be noted.

TABLE II

Operating conditions: $T \approx 280^\circ\text{C}$ $P = 40$ bars
 Space velocity = 5 $\text{H}_2/\text{HC} (1/1) = 150$
 H_2S in the recycle gas : 2000 ppm

Results after 120 hours of test.

Product	Catalyst	A	B	C	D	E	F	G	H	I	I'
% Sulfur		0.024	0.02	0.003	0.005	0.027	0.008	0.0005	0.001	0.0005 (= 5 ppm)	0.0012
Bromine number		37	36.5	35	36	37.5	37	11	8	0.2	33.9
O.N. research		92	92	91.5	91.5	92.5	92	87	86	83	89.2

The charge treatment with the catalysts G, H and I is repeated, but the operating conditions are adapted to decrease the hydrogenation rate. The selected operating conditions are as follows:

$T = 270^{\circ}\text{C}$ $VVH = 10$ H_2S in the recycle gas = 2000 vpm

$P = 40$ bars $\text{H}_2/\text{HC} = 150$ 1/1

5 The following results, reported in Table III, are obtained after 120 hours of test.

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TABLE III

Catalysts Products	I	G	H
% sulfur	0.0084	0.0084	0.0113
Bromine number	5	23	21
O.N. research clear	85	90	89.5

These results show that, in spite of the modified operating conditions, the selectivities obtained with the catalysts G, H and I are still far lower than those achieved with the catalysts A, B, C, D, E and F, as concerns the decrease of the octane number in the course of the treatment; in other words, the results reported in Table III show that a conventional catalyst (with a ratio R not conforming with the invention), when used under milder conditions as in the prior art, cannot yield a so satisfactory

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desulfurization

hydrogenation

ratio as the catalysts of the present invention, themselves used in these mild conditions.

EXAMPLE 3

15 The catalytic cracking gasoline whose specifications are given in the example 2 is treated with hydrogen, but the operation is continued for 650 hours to appreciate the stability of the operation. The results are given in Table IV. It is observed that the catalysts A, B, C are more stable than the catalysts G and H whose ratio R is 0.325, which are themselves more stable than the catalyst I whose ratio R is also 0.325, but which is prepared from an alumina of large surface and of a far greater acidity than the aluminous carrier of low surface used for manufacturing the catalysts A, B, C, G and H.

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The results obtained with a too high H_2S content of the recycle gas (6,000 vpm) are given in Table V.

TABLE IV

Operating conditions: P = 40 bars Space velocity = 5 H₂/HC = 150 l/l
 T = 280 °C H₂S in the recycle gas = 2000 vpm

CATALYSTS	A	B	C	G	H	I
Cycle time (hours)	120-340-650	120-340-650	120-340-650	120-340-650	120-340-650	120-340-650
S (ppm)	240 263 251	200 207 213	30 37 38	5 11 15	10 13 20	5 17 23
Bromine number	37 37.5 37	36.5 36.5 36	35 34.5 35.5	11 14 16	8 12 14	0.2 3 11
O.N. research	92 92 92	92 92 91.5	91.5 91 91.5	87 87.5 87.5	86 87 87	83 83 86

TABLE V

Same operating conditions as in Table IV, except H₂S content of the recycle gas : 6000 vpm

CATALYSTS	A	B	C
Cycle time (hours)	650	650	650
S (ppm)	480	380	70
Bromine number	38.5	38	36.5
O.N. research	92	92	92

CLAIMS

1. Process for reducing the sulfur or sulfur compound content of a catalytic cracking effluent containing 15 to 45% by weight of olefins without substantial decrease in the octane number of said effluent and without decreasing the bromine number of this effluent by more than 10%, the process
 5 being performed in a reaction zone in the presence of hydrogen at a temperature in the range 260 to 310°C and in the presence of a catalyst comprising (i) a non-acidic carrier that is (a) silica, (b) alumina of specific surface lower than 70 m²/g and of the α -alumina or tetragonal γ -alumina type, (c) cobalt, nickel, barium, magnesium or calcium aluminate having a specific surface lower than 130 m²/g, or (d)
 10 an alumina that has been heated in an autoclave and whose specific surface is lower than 135 m²/g and (ii) cobalt together with tungsten and/or molybdenum, the total weight of the cobalt, tungsten and/or molybdenum, expressed as oxide, being from 2 to 30% of the total catalytic mass, the atomic ratio

$$R = \frac{\text{cobalt}}{\text{cobalt} + (\text{molybdenum and/or tungsten})}$$

being higher than 0.55.

2. A process according to Claim 1, in which the catalyst contains, by weight, 8 to 25% of cobalt, and tungsten oxides or 8 to 25% of cobalt and molybdenum oxides, R being from 0.6 to 0.9.
 3. A process according to Claim 2, in which the catalyst contains cobalt and tungsten.
 4. A process according to Claim 1, in which the catalyst carrier is alumina and the specific surface of the catalyst is lower than 70 m²/g.
 5. A process according to Claim 1, in which the catalyst carrier is an aluminate of cobalt, nickel, barium, magnesium or calcium having a specific surface lower than 130 m²/g, and in which the specific surface of the catalyst is lower than 130 m²/g.
 6. A process according to Claim 5, in which the aluminate is calcium aluminate.
 7. A process according to any one of Claims 1 to 6, in which the ratio R is between about 0.7 and 0.8.
 8. A process according to any one of the preceding claims, in which the reaction effluent is cooled so as to obtain, by condensation, a hydrocarbon fraction distilling in the gasoline range, and a gas fraction of high hydrogen content, which is at least partly recycled to the reaction zone, the recycled portion of the fraction of high hydrogen content containing 150 to 5000 parts per million by volume of hydrogen sulfide.
 9. A process according to Claim 8, in which the recycled portion of the fraction of high hydrogen content contains 200 to 4000 parts per million by volume of hydrogen sulfide.
 10. A catalyst as defined in any one of Claims 1 to 7.
 11. A process as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples.
 12. A desulfurized catalytic cracking effluent obtained by a process as claimed in any one of Claims 1 to 9 and 11.